

# Effects of Supercacid Depolymerization and Catalytic Hydrogenation on Pyrolysis Reactivity of Illinois #6 Coal

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## INTRODUCTION

Pretreatments under mild conditions do not substantially alter the structure of coal and increase its extractability with organic solvents [1,2]. Up to 80 wt% of Yallourn coal, which had been oxidized at 60°C with aqueous  $H_2O_2$  in the presence of 1-propanol, was solubilized in ethanol [1]. The ethanol soluble fraction was further hydrogenated using a  $Ru/Al_2O_3$  catalyst in a mixed solvent of ethanol and acetic acid at 120°C for 12-72 h at a hydrogen pressure of 10 MPa [2], to give a yellowish white solid (hydrogenated white coal). This catalytic hydrogenation altered the aromatic structure of the coal, in part, and increased its reactivity with respect to pyrolysis. However, the  $H_2O_2$  oxidation was not effective in increasing the extractability of bituminous coals.

Shimizu et al. [3,4] depolymerized a subbituminous coal using a superacid at 150°C. This was a unique process which greatly increased the solubility of coal. In the present study, Illinois #6 coal was depolymerized using the superacid, trifluoromethanesulfonic acid ( $CF_3SO_3H$ , hereafter, referred to TFMS), in the presence of solvents at 120°C, and the treated coal was then extracted with tetrahydrofuran (THF). The THF solubilized coal was then hydrogenated over a Ru catalyst at 120°C for 48 h under a hydrogen pressure of 10 MPa. Changes in coal structure and pyrolysis reactivity by the combination of superacid treatment and catalytic hydrogenation were then examined.

## EXPERIMENTAL

**Depolymerization via Treatment with Supercacid Followed by THF Extraction:** Figure 1 shows the procedure for superacid treatment and THF extraction of Illinois #6 coal. 1 g of the coal, which was pulverized to 74-125  $\mu m$  in size, 3-5 mL of TFMS, and 13 mL of a solvent were mixed in an autoclave of 25 mL. Toluene, methylcyclopentane or isopentane were used as the solvent, and the suspension was stirred at 120°C for 3 h [3]. After the depolymerization, the product was neutralized with an aqueous solution (5 wt%) of  $Na_2CO_3$ . The precipitate was washed with water and extracted with THF under ultrasonic irradiation at room temperature. The mixture was then separated into THF-soluble ( $TS_d$ ) and THF-insoluble (TI) fractions by centrifugation. The  $TS_d$  fraction was then subjected to hydrogenation. The raw coal was also

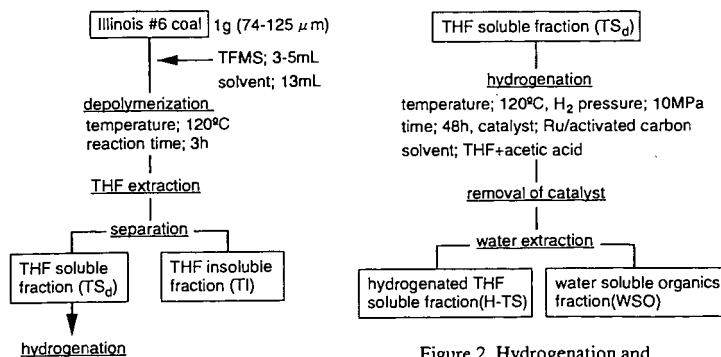


Figure 1. Depolymerization and fractionation procedure.

Figure 2. Hydrogenation and fractionation procedure.

extracted with THF, and the THF soluble fraction was subjected to further characterization. The TS fraction of the raw coal is hereafter referred to as the TS<sub>d</sub> fraction.

**Hydrogenation of THF Extract:** Figure 2 illustrates the procedure used for the hydrogenation of the TS<sub>d</sub> fraction. A ruthenium-supported activated carbon catalyst (metal content = 5 wt%, Wako Chemical) was used for the hydrogenation. 1 g of the TS<sub>d</sub> fraction was dissolved in a mixture of 8 mL of acetic acid and 6 mL of THF in a 25 mL autoclave equipped with a magnetic stirrer, and hydrogenated using 1.5 g of the catalyst at 120°C for 48 h under a hydrogen pressure of 10 MPa. After the removal of the catalyst by filtration, the solvent was evaporated. The product was then extracted with water under ultrasonic irradiation, leading to a hydrogenated, THF-soluble (H-TS) fraction and a water-soluble organic (WSO) fraction. Each fraction was dried at 70°C for 6 h under vacuum, and the yields were determined gravimetrically.

**Structural Analysis and Flash Pyrolysis of Products:** The H/C atomic ratio of the coals was evaluated by elemental analysis, and the molecular weight was determined by GPC analysis described previously [2]. The hydrogen distribution and aromaticity ( $f_a$ ) were estimated by <sup>1</sup>H-NMR spectroscopy and elemental analysis using the Brown-Lander equation [5]. The thermal reactivity of the coals was evaluated by flash pyrolysis at 764°C under an inert atmosphere using a Curie-point pyrolyzer (CPP, Japan Analytical Industry, JHP-22). Inorganic gases (IOG; CO, CO<sub>2</sub>, H<sub>2</sub>O and H<sub>2</sub>) and hydrocarbon gases (HCG; C<sub>1</sub>-C<sub>5</sub>) were analyzed using gas chromatographs (GC) equipped with TCD and FID detectors. The tar fraction was analyzed using a CPP connected to a GC interfaced with a mass spectrometer (GC/MS, Shimadzu, QP-5000) [6].

## RESULTS

The TS<sub>d</sub> and TS<sub>d</sub> fractions were recovered as solids after the removal of the solvent, while the H-TS fraction was a viscous black liquid. Figure 3 shows the yields of the TS<sub>d</sub>, TS<sub>d</sub> and TI fractions. The yields are expressed in wt% of the mass of the dry raw coal. The TS<sub>d</sub> yield, which was 14

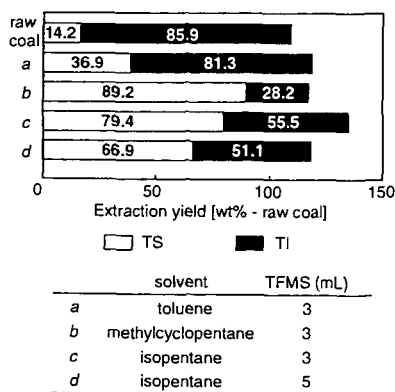


Figure 3. Yields of TS and TI fractions by depolymerization using TFMS.

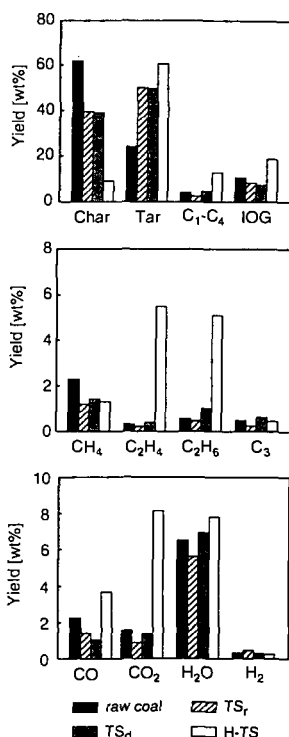


Figure 4. Product distributions of flash pyrolysis.

wt% for the raw coal, was increased by the depolymerization to 89 wt% for the case of methylcyclopentane, and 79 wt% for isopentane. Figure 4 shows the product distributions of the flash pyrolysis for the raw coal, the TS<sub>r</sub> and TS<sub>d</sub> fractions, and the H-TS fraction. The yields are expressed based on the initial mass of each sample used for pyrolysis. The char yield was 62 wt% for the raw coal, 40 and 38 wt% for the TS<sub>r</sub> and TS<sub>d</sub> fractions, respectively, and 5 wt% for the H-TS fraction. The tar yield was increased from 24 wt% for the raw coal to 61 wt% for the H-TS. The total yield of hydrocarbon gases, which were rich in ethylene and ethane, was increased as a result of the hydrogenation. The yields of CO, CO<sub>2</sub> and H<sub>2</sub>O were increased, while the yield of H<sub>2</sub> remained unchanged by the hydrogenation.

Table 1 shows the elemental analysis of the raw coal and the TS<sub>r</sub>, TS<sub>d</sub> and H-TS fractions, as well as the molecular weight of the TS<sub>r</sub>, TS<sub>d</sub> and H-TS fractions. The H/C atomic ratio was increased from 0.89 for the raw coal to 1.52 for the H-TS fraction. The molecular weight of the H-TS fraction at the peak of the elution curve was approximately 1000. Table 2 shows the hydrogen distribution, as well as the aromaticity, of the TS<sub>r</sub>, TS<sub>d</sub> and H-TS fractions, as determined by H-NMR spectroscopy. The depolymerization resulted in an increase in the H<sub>β</sub> and H<sub>γ</sub> of the TS<sub>r</sub> fraction. The hydrogenation of the TS<sub>d</sub> fraction resulted in a decrease in the H<sub>ar</sub>, H<sub>a</sub> and f<sub>a</sub>, and an increase in the H<sub>β</sub>. The H<sub>γ</sub> remained unchanged by the hydrogenation.

The tar component, obtained by the pyrolysis of the H-TS fraction at 764°C, contained approximately 40 components. The unit structures of 6 major components were analyzed by GC/MS, elemental analysis, molecular weight and hydrogen distribution. As shown in Figure 5, these species were composed of 1-3 rings, suggesting a partial hydrogenation of the coal structure. The yield of these species was 14 wt% for (A), 13 wt% for (B), 11 wt% for (C), 7 wt% for (D), 8 wt% for (E) and 4 wt% for (F) with respect to the initial mass of the H-TS.

## DISCUSSION

The Illinois #6 coal, which was depolymerized using TFMS in the presence of methylcyclopentane, was solubilized in THF at a yield of 89 wt%. As shown in Table 2, the increase in the H<sub>β</sub> and H<sub>γ</sub> after superacid treatment suggests that alkyl groups, derived from the solvent, are introduced into the coal structure [3]. The decreases in H<sub>ar</sub>, H<sub>a</sub> and f<sub>a</sub> indicate that the aromatic rings in the coal structure are hydrogenated over the Ru catalyst. The increase in H<sub>β</sub>, which is assigned to methylene and alicyclic hydrogens, is also indicative of the hydrogenation of the aromatic structure of the coal. The H<sub>γ</sub>, which is assigned to methyl hydrogens of the TS<sub>d</sub>, remains unchanged by the hydrogenation, suggesting that side chains are not greatly decomposed during the hydrogenation.

No differences in pyrolysis reactivity were observed between TS<sub>r</sub> and TS<sub>d</sub>. The HCG yield is increased by only 2 wt% by depolymerization. Thus the superacid treatment leads to an increase in the amount of extracts without altering the pyrolysis reactivity of the TS<sub>r</sub> fraction. The yield of volatile matters is increased by the hydrogenation from 62 wt% for the TS<sub>d</sub> fraction to 95 wt% for the H-TS fraction. Assuming that the decrease in the f<sub>a</sub> is caused by the hydrogenation of aromatic rings, 21 mol% of the aromatic carbons in the coal are converted to alicyclic carbons.

## CONCLUSIONS

THF-solubilized coal was depolymerized with TFMS and then hydrogenated over a Ru catalyst in a mixed solvent of THF and acetic acid at 120°C. The pyrolysis reactivity of the THF-

Table 1. Elemental Analysis and Molecular Weight of the Raw Coal, TS<sub>r</sub>, TS<sub>d</sub> and H-TS Fractions

| sample          | C              | H   | N   | (O+S) diff | H/C  | O/C  | Mw <sup>a</sup> |
|-----------------|----------------|-----|-----|------------|------|------|-----------------|
|                 | [wt% - d.a.f.] |     |     |            |      |      |                 |
| raw coal        | 74.5           | 5.5 | 1.5 | 18.5       | 0.89 | 0.19 |                 |
| TS <sub>r</sub> | 75.3           | 5.5 | 1.4 | 17.8       | 0.88 | 0.18 | 3000            |
| TS <sub>d</sub> | 77.2           | 6.3 | 0.9 | 15.6       | 0.98 | 0.15 | 1500~2000       |
| H-TS            | 68.7           | 8.7 | 0.1 | 22.5       | 1.52 | 0.25 | 1000            |

<sup>a</sup> molecular weight

Table 2. Hydrogen Distribution and Aromaticity of TS<sub>r</sub>, TS<sub>d</sub> and H-TS Fractions

| sample          | mol/100 mol of hydrogen |                |                |                | f <sub>a</sub> |
|-----------------|-------------------------|----------------|----------------|----------------|----------------|
|                 | H <sub>ar</sub>         | H <sub>α</sub> | H <sub>β</sub> | H <sub>γ</sub> |                |
| TS <sub>r</sub> | 25.3                    | 29.4           | 34.0           | 4.9            | 0.61           |
| TS <sub>d</sub> | 19.9                    | 22.5           | 39.8           | 11.2           | 0.60           |
| H-TS            | 10.1                    | 13.3           | 53.2           | 12.0           | 0.39           |

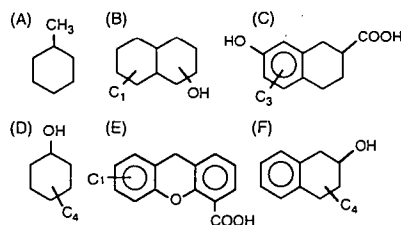


Figure 5. Unit structures of major compounds formed by pyrolysis of the hydrogenated TS fraction.

solubilized coal was increased by catalytic hydrogenation, which clearly altered the aromatic structure of the coal.

#### ACKNOWLEDGMENTS

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